

# **FLUORINE GAS TREATMENT OF WASHING MACHINE PARTS**

## **BACKGROUND OF THE INVENTION**

### **1. Field of the Invention**

5       The present invention pertains to the art of washing machines, specifically dishwashers and clothes washing machines, and, more particularly, to plastic washing machine parts having improved resistance to stains and a method of treating the plastic parts to improve stain resistance.

### **10   2. Discussion of the Prior Art**

Typically, interior walls of a dishwasher tub are formed of plastic, generally polypropylene. In addition, the use of plastic for the internal components of dishwashers, such as spray arms, is becoming increasingly popular due to the relatively low cost, lightweight, and flexibility of  
15   design offered by plastic. However, plastic dishwasher parts, as well as plastic food containers, are prone to staining by food residue. Plastic

dishwasher parts are particularly prone to red stains from processed tomato products, such as tomato sauce, ketchup, and spaghetti sauce. Red stains, technically known as carotenoid stains, are caused by lycopene in tomato products. Lycopene can be absorbed into plastic items and cannot be completely removed by dishwashing detergents.

Although reducing the ability of a part to be stained may be of interest in certain other fields, the problems associated with staining are of particular concern in connection with plastic dishwasher components. For instance, both a tub and door liner of a dishwasher are typically white in color. During use, if these components are discolored by tomato or other food product stains, the overall appearance of the dishwasher is degraded. Certainly, consumers do not want to put dishes to be cleaned in a dishwasher which has a soiled or otherwise stained washing chamber. As plates or bowls containing tomato or other high staining foods are oftentimes not rinsed prior to loading a dishwasher, the staining foods will tend to drip onto the inner components of the dishwasher. If these staining foods remain on the plastic components for any significant length of time prior to operating the dishwasher, a certain amount of staining is sure to occur. Of course, many of the dishwasher parts could be made from materials which would inherently resist staining, such as stainless steel. However, although a market exists for such high-end products, the need to provide a more economically feasible dishwasher leads to the increasing need to employ plastic parts. Some similar problems also exist in connection with clothes washing machines, specifically those incorporating plastic washing tubs or spinners, agitators and/or baffles. Certainly, unsightly stains on these components will lead to customer

dissatisfaction. Based on the above, there exists a need to make dishwasher parts from plastic that are more resistant to staining.

## **SUMMARY OF THE INVENTION**

The present invention is concerned with treating plastic  
5 components of a washing chamber with a fluorine-containing gas mixture  
in order to improve the stain resistance of plastic components. In  
accordance with the invention, the plastic components are placed in a  
reaction chamber into which a gas mixture containing fluorine and  
oxygen is introduced. The components and gas mixture remain in the  
10 chamber for a sufficient amount of time for the gas mixture to react with  
the plastic components, such that the gas mixture modifies at least a  
surface layer of the plastic components.

It has been found that treating washing machine components in this  
manner significantly alters the resistance of the plastic components to  
15 staining, even staining associated with tomato based products, which is of  
particular concern in the art of dishwashers. In connection with the  
invention, plastic dishwasher components that may be treated by the gas  
mixture include: dishwasher tubs, door liners, spray arms, racks, conduits,  
silverware baskets, pump housings, and the like. For clothes washing  
20 machines, plastic tubs or spinners, agitators, baffles and the like can be  
advantageously treated. That is, any plastic component which is arranged  
in a washing chamber so as to be subject to staining by foods or soiled  
clothes may be treated in accordance with the present invention.

Additional objects, features and advantages of the present invention will become more readily apparent from the following detailed description of preferred embodiments of the invention.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

5        Figure 1 is a view of a dishwasher containing plastic parts treated in accordance with the present invention;

Figure 2 is a side view of a plastic dishwasher part treated in accordance with the invention; and

Figure 3 is schematic representation of a treatment system  
10    employed in connection with the invention.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

With initial reference to Figure 1, the invention will be described with particular reference to a dishwasher 2. As shown, dishwasher 2  
15    includes a tub 5, which is injection molded of plastic, preferably polypropylene, so as to include integral bottom, side, rear and top walls 8-12 respectively. Within the confines of walls 8-12, tub 5 defines a washing chamber 14 within which soiled kitchenware is adapted to be placed upon shiftable upper and lower racks (one of which is indicated at  
20    15), with the kitchenware being cleaned during a washing operation in a

manner widely known in the art. Tub 5 has attached thereto a frontal frame 16 which pivotally supports a door 20, having an outer panel 21 and an inner liner 22, used to seal chamber 14 during a washing operation. In connection with the washing operation, door 20 is  
5 preferably provided with a detergent tray assembly 23 within which a consumer can place liquid or particulate washing detergent for dispensing at predetermined cycles of the washing operation. Of course, dispensing detergent in this fashion is known in the art such that this arrangement is only being described for the sake of completeness.

10           Disposed within tub 5 and, more specifically, mounted within a central opening formed in bottom wall 8 of tub 5, is a pump and filter assembly 30. Extending about a substantial portion of pump and filter assembly 30, at a position raised above bottom wall 8, is a heating element 44. In a manner known in the art, heating element 44 preferably  
15 takes the form of a sheathed, electric resistance-type heating element.

          In general, pump and filter assembly 30 is adapted to direct washing fluid to a lower wash arm 47 and an upper wash arm (not shown). Dishwasher 2 has associated therewith a drain hose 85 including at least one corrugated or otherwise curved portion 89 that extends about  
20 an arcuate hanger 92 provided on an outside surface of side wall 10. Drain hose 85 is also preferably secured to tub 5 through various clips, such as that indicated at 94. In any event, in this manner, an upper loop is maintained in drain hose 85 to assure proper drainage in a manner known in the art. Actually, a detailed description of the exact structure and  
25 operation of pump and filter assembly 30 of dishwasher 2 does not form part of the present invention, but is rather set forth in pending U.S.

Application Serial No. 10/186,739 entitled "Dishwasher Pump and Filtration System" filed July 2, 2002, incorporated herein by reference. In addition, a silverware basket 100 is shown positioned in rack 15 in a manner known in the art.

5           The present invention is actually directed to providing various components of dishwasher 2 with an increased resistance to stains. In general, the process includes exposing the dishwasher parts to a fluorine-containing gas mixture for an amount of time sufficient to allow the gas mixture to react with the plastic parts. The reaction that takes place  
10   between the plastic parts and the gas mixture modifies the surface of the plastic parts such that the parts exhibit the increased resistance to stains.

Essentially, any plastic dishwasher part that is susceptible to stains from contact with food residue may be treated by the process of the invention. The plastic dishwasher parts that may be treated include, but  
15   are not limited to, walls 8-12, a shiftable upper rack (not shown), shiftable lower rack 15, inner liner 22 of door 20, dispensing assembly 23, lower wash arm 47, an upper wash arm (not shown), at least the housing for pump and filter assembly 30, basket 100, and the like. However, for discussion purposes, reference will be made to Figures 2  
20   and 3 in discussing the treatment of a representative plastic dishwasher part which is generically referred to as plastic part 150. Preferably, plastic part 150 includes a main body 155 which is molded of polypropylene. Main body 155 has at least one surface 158 exposed to washing chamber 14.

The treatment in accordance with the invention includes placing plastic part 150 within a closed reaction chamber unit 160 having an internal reaction chamber 165 which can be selectively sealed by one or more doors 175. Reaction chamber 165 may be of any suitable size or shape to permit easy placement and removal of part 150. Further, reaction chamber 165 may be constructed from stainless steel or any suitable material known in the art. After placing part 150 into reaction chamber 165, the gas mixture is introduced into chamber 165 from a storage vessel 190. The gas mixture contains fluorine and may include other reactive gases, such as oxygen. Further, the gas mixture inevitably includes a quantity of inert gas, such as nitrogen. Preferably, fluorine makes up less than 10% of the gas mixture, with the remainder being a mixture of oxygen and nitrogen. In accordance with the most preferred embodiment of the invention, the reaction is carried out at a temperature of 30-70°C, most preferably about 45°C, and a pressure of 0.1-0.9 atm, most preferably about 0.5 atm.

Plastic part 150 remains in reaction chamber 165 for a sufficient amount of time for the fluorine and oxygen gases to react with at least an outer layer 158 of plastic part 150. More specifically, since part 150 is preferably formed of polypropylene, the fluorine and oxygen atoms from the gas mixture replace many of the hydrogen atoms located on outer layer 158 of the polypropylene part 150. Generally, the longer part 150 is exposed to the gas mixture in reaction chamber 165, the more hydrogen atoms will be replaced. Hence, longer exposure times lead to a greater depth of penetration of the reaction. Typically, surface 158 of plastic part 150 is sufficiently treated in 0.5-60 minutes. For example, walls 8-12 of chamber 14 are 90-120 mils in thickness. By placing walls 8-12 within

reaction chamber 165 containing the gaseous mixture for 10-20 minutes, the reaction will have penetrated walls 8-12 to 2,000 angstroms.

Treatment with the gas mixture in accordance with the invention is considered to be advantageous over plasma, corona, or flame treatments because the changes of surface 158 in plastic part 150 that result from the treatment are permanent due to the depth of penetration of the reaction. Following the treatment of plastic part 150, any remaining treatment gas and by-product gases are evacuated from reaction chamber 165, such as into containment vessel 195. These gases may be discarded or, more preferably, recycled. Alternatively, the gases may be used in a scrubbing process. Following removal from reaction chamber 165, plastic part 150 may be installed into dishwasher 2 without undergoing any additional processing. The following examples are presented to further illustrate the present invention and are not meant to be limiting:

#### EXAMPLE 1

Example 1 was carried out to measure the difference in the stain resistance of plastic dishwasher parts that have been treated with the gas mixture of the invention versus parts not treated with the gas mixture. An initial test was performed wherein two dishwashers were subjected to thirty wash cycles. Prior to the initial wash cycle, a meat and tomato sauce mixture was placed within the washing chamber of each dishwasher. More specifically, a standard soiling protocol test (ANSI/AHAM DW-1-1992) was modified by adding an additional 12 oz. can of tomato paste to the meat mixture. Additional amounts of the meat and tomato sauce mixture were added to the washing chambers between each wash cycle. No cleaning or other modification of the dishwashers



took place between cycles. One dishwasher included plastic parts which had been treated in accordance with the present invention and the other dishwasher included identical plastic parts which were not treated. The change in color of the plastic parts was measured after thirty wash cycles.

- 5 The change in color is indicated by  $\Delta E$ , which is a single number that defines an elliptical color difference around the product standard. As shown in Table 1, the color of the untreated dishwasher parts had changed by 18.2 as compared to a change of only 5.8 in the plastic parts treated by the fluorine gas mixture.

**Table 1. Color change ( $\Delta E$  value\*) after DW1 test.**

DW1	w/o treatment	w/ treatment
30 cycles	18.2	5.8

\* $\Delta E$ : a single number which defines an elliptical color difference around the product standard.

- 10 In addition, a brightness parameter (Y) of the dishwasher parts was measured after ten, twenty, and thirty dishwasher cycles. The brightness parameter is a measure of luminance, which is light intensity factored by the sensitivity of a normal human eye. Starting with a brightness parameter of 100 prior to the initiation of the first wash cycle, the results
- 15 are shown in Table 2. After ten wash cycles, the brightness parameter of the untreated parts was reduced to 71.6. After twenty wash cycles, the untreated parts again dulled to give a brightness parameter of 69.4. Following all thirty wash cycles, the brightness parameter of the untreated parts was 64.6. This is a decrease in brightness of 35.4 over
- 20 thirty wash cycles. However, the brightness parameter of the parts treated by the fluorine gas mixture was 81.9, 80.1, and 81.3 after ten, twenty and thirty wash cycles, respectively. Therefore, the total

reduction in brightness of the treated parts was only 18.7 over thirty wash cycles, as compared to 35.4 for the untreated parts.

**Table 2 - Brightness parameter (Y value\*\*) after DW1 test**

DW1	w/o treatment	w/ treatment
10 cycles	71.6	81.9
20 cycles	69.8	80.1
30 cycles	64.6	81.3

\*\* The brightness parameter (Y) is a measure of luminance, which is light intensity factored by the sensitivity of the normal human eye.

## EXAMPLE 2

In a second test, four plastic test samples, i.e., one untreated sample  
5 and three treated samples, were placed in a dishwasher soiled with a  
tomato mixture to demonstrate the stain resistance of plastic parts treated  
by the gas mixture. Initially, a color reading was taken of the one  
untreated sample and three treated samples. The first treated sample was  
treated with a gas mixture having 5% fluorine, 5% oxygen and 90%  
10 nitrogen. The second treated sample was treated with a gas mixture  
having 1% fluorine, 5% oxygen and 94% nitrogen. The third treated  
sample was treated with a gas mixture having 2% fluorine, 3% oxygen  
and 95% nitrogen. Each of the samples was placed within a dishwasher  
rack or silverware basket inside the washing chamber. A two cup  
15 microwavable bowl was used to measure ¼ cup of a meat mixture and ½  
cup of tomato sauce. A rubber spatula was used to scrape all of the  
tomato sauce out of a can. The mixture was then stirred and heated in a  
microwave for about two minutes before being poured onto the inner  
liner of the dishwasher door. In addition, the soiled bowl and spatula  
20 were placed within the dishwasher chamber. Two tablespoons of  
detergent were placed in the dispensing assembly and a normal wash

cycle was performed. The procedure was performed a total of three times. Between each cycle and following the completion of all cycles, color readings were taken for each of the samples. The results are indicated in Table 3 below.

**Table 3 - Color change after tomato stain test**

	$\Delta L$	$\Delta a$	$\Delta b$	$\Delta E^*$
PP – Untreated				
Before the test	3.11	0.30	0.88	-
After 1 <sup>st</sup> Cycle	6.25	9.99	9.50	13.34
After 2 <sup>nd</sup> Cycle	12.11	14.91	15.44	22.50
After 3 <sup>rd</sup> Cycle	7.30	12.35	26.44	24.00
Sample 1				
Before the test	4.24	0.33	0.23	-
After 1 <sup>st</sup> Cycle	4.75	1.00	0.55	0.90
After 2 <sup>nd</sup> Cycle	4.88	0.81	0.34	0.93
After 3 <sup>rd</sup> Cycle	4.86	0.62	0.55	0.72
Sample 2				
Before the test	5.25	0.19	1.79	-
After 1 <sup>st</sup> Cycle	5.06	0.99	0.25	1.75
After 2 <sup>nd</sup> Cycle	4.90	0.72	0.74	1.22
After 3 <sup>rd</sup> Cycle	4.81	0.69	1.32	0.81
Sample 3				
Before the test	4.32	0.23	0.88	-
After 1 <sup>st</sup> Cycle	5.06	0.89	0.30	1.15
After 2 <sup>nd</sup> Cycle	4.80	0.67	0.79	0.66
After 3 <sup>rd</sup> Cycle	4.68	0.72	1.50	0.87

$\Delta L$ : The change in lightness between treated sample after specified cycle and sample before test.

$\Delta a$ : The change in red/green tones between treated sample after specified cycle and sample before test.

$\Delta b$ : The change in yellow/blue tones between treated sample after specified cycle and sample before test.

$\Delta E^*$ : The total color difference between treated sample after specified cycle and sample before test.

In table 3, the first column,  $\Delta L$ , indicates a change in lightness in the samples before testing began and after the first, second and third wash cycles. The second column,  $\Delta a$ , indicates a change in red/green tones in the samples before testing began and after the first, second and third wash cycles. The third column,  $\Delta b$ , indicates a change in yellow/blue tones in the samples before testing began and after the first, second and third wash cycles. The last column,  $\Delta E^*$ , indicates the total color difference in the samples before testing began and after the first, second and third wash cycles. For example, the color of the untreated sample changed by 13.34 after the first cycle. After the second cycle, the color of the untreated sample had changed by a total of 22.50 and, after the third cycle, by a total of 24.00. This is a very significant change in color when compared to the changes in the treated samples, particularly the first treated sample which experienced color reading changes of 0.90, 0.93 and 0.72 after the first, second and third cycles, respectively.

In addition to the stain resistance aspects of the invention, the treated plastic machine components have been found to not develop carotenoid stains caused by foods that contain lycopene. The surfaces of the components also exhibit improved surface energy or wettability, as well as enhanced drying characteristics as water tends to spread out on the components instead of beading into large droplets. In any case, it should be readily apparent that treating plastic dishwasher components in accordance with the invention makes the components significantly more resistant to being stained from even the worst types of staining food substances typically experienced in connection with a domestic dishwasher. For a relatively minor incremental cost, various dishwasher components can be treated to provide a long-lasting, more aesthetically

appealing and overall hygienic washing chamber arrangement. In any case, although described with reference to a preferred embodiment of the invention, it should be readily understood that various changes and/or modifications can be made to the invention without departing from the spirit thereof. For instance, although the invention is seen to have particular use in connection with treating dishwasher components, other washing machine components can benefit from the invention for generally corresponding reasons. For example, clothes washing machine tubs or spinners can be made of plastic, as well as agitators and baffles located in the tubs. Treating these washing machine components in a corresponding manner can prevent staining from various soils removed from clothing, as well as dyes which are inherently drawn from certain clothing during washing operations. In general, the invention is only intended to be limited by the scope of the following claims.